OIPE JC57
APR 07 2003
PATENT & TRADEMARK OFFICE

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

#10
04/12/03
RECEIVED
TC 1700

In re Application of: Yoshikazu SANO et al.

Serial No.: 09/719,359 Group Art Unit: 1714

Filed: December 11, 2000 Examiner: SHOSHO, CALLIEE

For: PROCESS FOR PREPARATION OF PHENOL-MODIFIED ROSIN ESTER, PHENOL-MODIFIED ROSIN ESTER AND USE THEREOF

DECLARATION

Honorable Commissioner of Patents and Trademarks
Washington, D.C. 20231

Sir :

I, Yoshikazu SANO, hereby declare:

1) That I am one of the inventors of the instant invention, and

2) That the experiments given below were carried out under my general direction and supervision.

Experiments 1 to 4

(1) Experiment 1

A phenol-modified rosin ester as a binder for printing inks of the present invention was prepared in the same manner as in Example 1 in the specification of the present invention. The obtained rosin ester was found to have an acid value of 22 mg KOH/g, a weight average molecular weight of 43,000

(calibrated with polystyrene standard samples; the same is applied hereinafter), a softening point of 169°C (ring and ball method; the same is applied hereinafter), a nitrogen residue content of 200 ppm (measured by microanalysis of total nitrogen by catalyst oxidation conversion method; the same is applied hereinafter) and a solubility (25°C) of not less than 20 times when using "No.5 Solvent" (trade name, product of Nippon Oil Corporation) as a petroleum hydrocarbon solvent (boiling point range 276 to 313°C, aniline point 69°C).

(2) Experiment 2

(i) A pressure-resistant reactor (1.5 MPa) equipped with a stirrer, an internal pressure meter, a reflux condenser having a water separator and a thermometer was charged with 4,000 parts by weight of p-octylphenol and 1,050 parts by weight of 92% paraformaldehyde. The mixture was heated to 70°C in a closed reactor under an increased pressure to form a solution, and 500 parts by weight of triethylamine was added as a catalyst for conversion to resol. Then the mixture was heated to 145°C to undergo a reaction for 10 minutes, giving a solution of a resol phenol resin having a weight average molecular weight of 880 (solid content 96% by weight).

(ii) 1,800 parts by weight of gum rosin was charged into a reactor equipped with a stirrer, a reflux condenser having a water separator and a thermometer and was fused with heating

to 230°C in a nitrogen atmosphere. Then 170 parts by weight of pentaerythritol was added and homogeneously mixed, and 4 parts by weight of calcium hydroxide was added as an esterification catalyst. Thereafter the mixture was heated to 285°C. The water produced was collected by the reflux condenser having a water separator. A reaction was conducted at the same temperature for 8 hours and the reaction mixture was cooled to 250°C when the acid value reached not higher than 25 mg KOH/g. Subsequently 1,100 parts by weight of the resol phenol resin solution prepared in the above (i) (solid content 96% by weight) was added dropwise over a period of 4 hours at the same temperature. The mixture was held at the same temperature awhile, giving a phenol-modified rosin ester as a binder for printing inks of the present invention.

The obtained rosin ester was found to have an acid value of 17 mg KOH/g, a weight average molecular weight of 48,000, a softening point of 170.5°C, a nitrogen residue content of 780 ppm and a solubility (25°C) of not less than 20 times when using "No.5 Solvent".

(3) Experiment 3

A phenol-modified rosin ester as a binder for printing inks for comparison was prepared in the same manner as in Comparative Example 2 in the specification of the present invention. The obtained rosin ester was found to have an acid

value of 22 mg KOH/g, a weight average molecular weight of 43,000, a softening point of 172°C, a nitrogen residue content of 0 ppm and a solubility (25°C) of not less than 20 times when using "No.5 Solvent".

(4) Experiment 4

(i) The foregoing pressure-resistant reactor was charged with 4,000 parts by weight of p-octylphenol and 933 parts by weight of 92% paraformaldehyde. The mixture was heated to 70°C in a closed reactor under an increased pressure to form a solution, and 1,200 parts by weight of triethylamine was added as a catalyst for conversion to resol. Then the mixture was heated to 145°C to undergo a reaction for 10 minutes, giving a solution of a resol phenol resin having a weight average molecular weight of 930 (solid content 97% by weight).

(ii) 1,800 parts by weight of gum rosin was charged into the foregoing reactor and was fused with heating to 230°C in a nitrogen atmosphere. Then 170 parts by weight of pentaerythritol was added and homogeneously mixed, and 4 parts by weight of calcium hydroxide was added as an esterification catalyst. Thereafter the mixture was heated to 285°C. The water produced was collected by the reflux condenser having a water separator. A reaction was conducted at the same temperature for 8 hours and the reaction mixture was cooled to 250°C when the acid value reached not higher than 25 mg KOH/g.

Subsequently 1,100 parts by weight of the resol phenol resin solution prepared in the above (i) (solid content 97% by weight) was added dropwise over a period of 4 hours at the same temperature. The mixture was held at the same temperature awhile, giving a phenol-modified rosin ester as a binder for printing inks for comparison.

The obtained rosin ester was found to have an acid value of 13 mg KOH/g, a weight average molecular weight of 40,000, a softening point of 169.5°C, a nitrogen residue content of 1,520 ppm and a solubility (25°C) of not less than 20 times when using "No.5 Solvent".

Performance Test

Each of the phenol-modified rosin esters prepared in the Experiments 1 to 4 was employed as a binder for printing inks so as to prepare black ink and red ink as described below. Then, the produced black inks and red inks were tested for performance.

(1) Preparation of Black Ink

A varnish was prepared by mixing 43 parts by weight of each of the phenol-modified rosin esters prepared in the foregoing Experiments 1 to 4 with 20 parts by weight of linseed oil and 45 parts by weight of "AF Solvent No.6" (trade name, a product of Nippon Oil Corporation) at 180°C to form a solution.

Then, 0.5 part by weight of ethylacetoacetate aluminum diisopropylate (trade name "ALCH", product of Kawaken Fine Chemicals Co., Ltd.) was added to 100 parts by weight of the varnish. The mixture was reacted at 190°C for 1 hour to give a varnish gel. Black ink was prepared by milling the varnish gel with a three-roll mill using the following components in the proportions shown below:

Carbon black	18 parts by weight
Foregoing varnish gel	57-67 parts by weight
"AF Solvent No.6"	14-24 parts by weight
Drier	1 part by weight

The ink thus obtained was suitably adjusted to a tack value of 8.5 ± 0.5 and a flow value of 18 ± 0.5.

"MA7" (trade name, a product of Mitsubishi Chemical Corporation) was used as the carbon black and cobalt naphthenate was used as the drier.

(2) Performance Test of Black Ink

Each of the black inks prepared in the above was tested for performance in respect of gloss, resistance to emulsification, resistance to misting, drying time and resistance to smudging on printed paper sheets in accordance with the method described on Page 28, Line 21 to Page 30, Line 21 in the specification of the present invention.

Performance test was also conducted in respect of the

fluidity with the following method.

Fluidity: In an atmosphere at 25°C, 0.13 ml of the black ink was put on a glass plate held at an angle of 60 degrees to the level surface. The fluidity was determined by measuring length (mm) which the black ink flowed in 60 minutes. Black inks having high fluidity are preferable as is the case with black inks used in a printing machine actually operated.

The test results are shown in Table 1.

Table 1

Phenol-modified rosin ester as a binder for printing inks					
Experiment No.		1	2	3	4
Nitrogen residue content (ppm)		200	780	0	1,520
Performance of black ink	Gloss (%)	62	63	57	62
	Emulsification ratio (%)	28	32	45	50
	Resistance to misting	A	A	A	A
	Drying time (hr)	4.0	4.0	4.0	5.0
	Resistance to smudging on printed paper sheets	A	A	A	B
	Fluidity (mm)	250	250	130	245

(3) Preparation of Red Ink

Red ink was prepared using each of the phenol-modified rosin esters prepared in the foregoing Experiments 1 to 4 in accordance with the method described on Page 27, Line 4 from

the bottom to Page 28, Line 20 in the specification of the present invention.

(4) Performance Test of Red Ink

Each of the red inks prepared in the above was tested for performance in the same manner as in the black inks in respect of gloss, resistance to emulsification, resistance to misting, drying time, resistance to smudging on printed paper sheets and fluidity.

The test results are shown in Table 2.

Table 2

Phenol-modified rosin ester as a binder for printing inks					
Experiment No.		1	2	3	4
Nitrogen residue content (ppm)		200	780	0	1,520
Performance of red ink	Gloss (%)	70	72	62	70
	Emulsification ratio (%)	40	40	52	60
	Resistance to misting	B	B	B	B
	Drying time (hr)	5.0	5.0	5.0	5.5
	Resistance to smudging on printed paper sheets	A	A	A	B
	Fluidity (mm)	280	290	250	300

Consideration of Results

As is evident from Tables 1 and 2, when black inks and

red inks were prepared using the phenol-modified rosin esters that served as a binder of the present invention in Experiments 1 and 2, which have a nitrogen residue content in a specific range defined by the present invention, the prepared black inks and red inks of the present invention were of high gloss and high fluidity, and were excellent in resistance to emulsification (emulsification ratio) and resistance to smudging on printed paper sheets.

On the other hand, when black ink and red ink were prepared using the phenol-modified rosin ester that served as a binder for comparison in Experiment 3, in which no nitrogen residue content was detected, the prepared black ink and red ink were of low gloss and had an increased emulsification ratio, and the fluidity was sharply reduced in the black ink, as compared with each of the inks of the present invention.

When black ink and red ink were prepared using the phenol-modified rosin ester that served as a binder for comparison in Experiment 4, which had a nitrogen residue content beyond the range defined by the present invention, the prepared black ink and red ink undesirably presented an increased emulsification ratio, a prolonged drying time and the occurrence of smudging on printed paper sheets, as compared with each of the inks of the present invention.

It is clear that the binder for printing inks of the present invention which contains a phenol-modified rosin ester

having a nitrogen residue content in a specific range defined by the invention achieves excellent performance as a binder for printing inks. In other words, inks prepared using the same exhibit superior printability.

* * * * *

I, the undersigned, declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Date: March 26, 2003

Yoshikazu Sano

Yoshikazu SANO